GREAT LAKES

INTEGRATED ATMOSPHERIC DEPOSITION NETWORK (IADN)

DATA REPORT 1990 - 1992

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1. INTRODUCTION

1.1 Purpose

The purpose of this report is to summarize data from the first samples collected from the U.S. sampling stations in the Integrated Atmospheric Deposition Network (IADN) from October 1990 through December 1992.

1.2 Background

The Integrated Atmospheric Deposition Network is a joint effort of the United States and Canada to measure atmospheric deposition of toxic materials to the Great Lakes. It was mandated by Annex 15 (Airborne Toxic Substances) of the Great Lakes Water Quality Agreement (GLWQA) between the United States and Canada. The GLWQA was originally signed in 1972, and amended in 1978 and again in 1987, when Annex 15 was added among others. The network also fulfills the requirements of section 112 (m) of the U.S. Clean Air Act Amendments (CAAA) of 1990, the Great Waters Program, which calls for a Great Lakes atmospheric deposition network.

The plan for development of the new network was approved in 1990 (Canada/U.S. Coordinating Committee on Annex 15, 1990). Measurements of the following toxic chemicals were to be begun during Phase I (1991 and 1992): total polychlorinated biphenyls (PCBs) and major congeners, the alpha and gamma isomers of hexachlorocyclohexane (HCH), polyaromatic hydrocarbons (PAHs) (with B(")P as the goal), and lead (Pb). Those toxic compounds included as a second priority, and known to need considerable methods development, included chlorinated pesticides such as DDT and its metabolites, as well as chlordane, nonachlor, heptachlorepoxide, methoxychlor, dieldrin, HCB, and endrin. Also in the second-priority group were the trace metals arsenic, selenium, cadmium, and mercury.

The plan called for installation of one master (research-grade) sampling station on each of the Great Lakes by the end of 1992, but this schedule was advanced by one year to meet the requirements of the Great Waters Program in the 1990 CAAA, which required one sampling site on each lake by the end of 1991. The plan also calls for two or more satellite (routine) sites on each of the Great Lakes, plus one or more background stations. Plans for installation of satellite sites have not yet been implemented.

The master stations operate two or more of the primary network samplers to provide the sampling replication necessary to determine sampling and analytical precision. They typically provide enough space and electric power to accommodate additional research. The satellite stations are expected to include single samplers of the same types used at the master stations.

All sampling and analytical operations are governed by the Quality Assurance Project Plan (QAPjP) for the work (Gatz *et al.,* 1993). Details of analytical methods are given by Willett and Basu (1993) and are summarized below.

1.3 Scope

This report contains chemical measurements and meteorological observations from sampling

sites at Eagle Harbor, Michigan, on Lake Superior; Sleeping Bear Dunes National Lakeshore near Empire, Michigan, on Lake Michigan; and Sturgeon Point near Evans Center, New York, on Lake Erie. It also contains results for samples collected for comparison with other participants at the Canadian Point Petre site. A separate report will cover Canadian results from the sites at Point Petre on Lake Ontario, and Burnt Harbor on Lake Huron. Figure 1 shows the locations of all IADN sampling sites.

Overall, this report covers the period from October 1990 through December 1992. However, no sites were operational during this entire period. Available results are included for the period during which each site was operational. Results available from samples analyzed through the end of May 1993 are included. Analyses for some samples collected in 1991 and 1992 were not yet completed when this report was prepared. Results from these additional analyses will be included in subsequent reports.

Analyte groups included in this report include PCBs, chlorinated pesticides, PAHs, and trace metals in air. Details of the specific compounds or congeners included are given below. Interpretation of these data and the joint U.S.-Canada data set will be carried out later and reported in subsequent publications. A summary of quality assurance results is presented in Appendix B; complete quality assurance information

is given in a companion report (Harlin *et al.*, 1994).

Figure 1. IADN site locations

2. METHODS

2.1 Field Sampling Methods

2.1.1 Meteorological Methods

Each site has an instrumented 10-meter (m) meteorological tower with the following meteorological instruments: wind speed and wind direction sensors (Met-One, Grants Pass, OR) at a height of 10 m; a pyranometer (model LI-200SZ, Li-Cor, Lincoln, NE); and temperature (Fenwal Electronics UUT51J1 thermistor) and relative humidity sensors (Phys-Chemical Research PCRC-11 RH sensor) at a height of 2 m. A standard Belfort raingage (Belfort Instrument, Baltimore, MD) equipped with a Nipher wind shield is also located at each site. Outputs of all of the meteorological sensors are automatically accessed every 6 seconds using a datalogger (Campbell Scientific, model 21X, Logan, UT) and recorded as hourly average values. The data are recorded on an internal chip in the datalogger. They are either transferred to a cassette data tape that is mailed to the Illinois State Water Survey (ISWS) (i.e., at Sturgeon Point) or accessed and downloaded by ISWS directly using a telephone and modem (Eagle Harbor and Sleeping Bear Dunes).

An extra set of instruments is maintained for the meteorological towers. The instruments are replaced and returned to the manufacturer annually for reconditioning and recalibration. The Belfort raingage is calibrated quarterly using a standard weight set.

2.1.2 Sampling Methods for Organic Compounds in Precipitation

Sampling columns are prepared in the laboratory by packing a 30x2-centimeter (cm) glass column with a water slurry of cleaned XAD-2 resin to give a final bed height of about 10 cm. About 2 cm of packed glass wool is placed in the column before the slurry is added and on top of the resin bed. The ends of the columns are sealed with threaded Teflon plugs and PEFTE O-rings. The entire column is wrapped in aluminum foil for shipment. The foil remains in place during sampling to exclude light. When the columns are installed at the sites, the Teflon fittings are removed and the column is connected to the outlet of the collection funnel and to a valve fitting that controls flow from the column. The flow rate is set at 10 to 15 milliliters (mL) per minute.

Precipitation is collected using a commercial version of a wet-only sampler (MIC B,Thornhill, Ont.) developed by the National Water Research Institute in Canada (Strachan and Huneault, 1984). The samplers (figure 2) have polished stainless steel inlet surfaces with cross-sectional areas of 0.212 m^2. The operation of the samplers is automatically monitored by the datalogger, which records the time and duration that the collection funnel is uncovered. The samplers were modified for all-weather operation by enclosing and insulating the space beneath them. The temperature in the enclosure is maintained at 10 to

15EC by a small space heater, which provides sufficient heat to the catch basin to melt collected snow without heating the surface any more than necessary. Rain or melted snow passes by gravity flow through a sampling column containing about 7 grams (g) of cleaned XAD-2 resin (section 2.2.1.2). Glass wool plugs above and below the XAD-2 resin trap the particles in the sample. The end of the outlet tube from the column is held above the level of the XAD-2 resin so that the resin remains wet throughout the sampling period. In some cases, whole rain samples were transferred to clean

Figure 2. Schematic of MIC precipitation sampler

4-L amber bottles and shipped to the ISWS lab. Organics in these samples were extracted using C-18 EmporeJ disks (Analytichem International, Harbor City, CA). This method was used at Pt. Petre between October, 1990 and December, 1991 and at Eagle Harbor from November, 1990 to August, 1991. All other precipitation samples were collected using XAD columns as described above. Duplicate samples are taken at 28-day intervals. All valid duplicate samples were analyzed. At the end of each sampling cycle, the collection surfaces are rinsed with 200 mL of deionized water. During the rinsing process, the surfaces are also wiped with one quarter of an 8x10-inch glass fiber filter (GFF) to remove any adhering particles. These rinsings are allowed to pass over the XAD-2 resin and glass wool plugs before the column is removed from the sampler for shipment to the lab. The filter is placed in a clean glass jar with a Teflon-lined cap and is also sent to the laboratory with the column. Upon receipt at the laboratory, the XAD-2 and glass wool plugs are removed from the column; most of the water is removed by vacuum filtration using a filter flask and a small circle of glass fiber filter. Acetone is used to transfer the dried XAD-2, glass wool plugs, and filter circle to the glass jar containing the filter wipe. The jars are stored at -20EC before extraction. Everything in the jar is extracted as one sample (section 2.2.2.1).

2.1.3 Sampling for Trace Metals in Precipitation

The three IADN sites in the United States are also sites in the Great Lakes Acid Deposition (GLAD) network and are equipped with standard wet-only AeroChem Metrics samplers. Weekly precipitation samples are collected in new polyethylene bags and transferred to clean polyethylene bottles (USEPA, 1990). These samples are shipped to the U. S. Environmental

Protection Agency's (USEPA) Central Analytical Lab at the Great Lakes National Program Office in Chicago for analysis of trace metals and major ions. The results of these analyses will be reported elsewhere by the USEPA. During the summer of 1993, new precipitation samplers with all-Teflon sampling trains were installed at the U.S. IADN sites. Methods and results for these samplers will be described in the next data report.

2.1.4 Sampling Methods for Organic Compounds in Air

Samples of both airborne particles and airborne organic vapors are collected. Particles are collected on commercial glass fiber filters (Whatmann EPM 2000, Whatman, Ltd, Maidstone, UK). These filters are numbered, preweighed after equilibration at 50 percent relative humidity for 24 hours, and individually wrapped in aluminum foil before being shipped to the field. The vapor trap consists of a stainless steel cartridge 8.7 cm in diameter and 4.4 cm thick, containing between 35 and 45 g of cleaned XAD-2 resin. For some samples, we used glass cartridges containing precleaned polyurethane foam (PUF) plugs instead

of XAD-2 cartridges. The PUF plugs are 8.7 x 10 cm. Precleaning of PUF and XAD-2 is described in section 2.2.1.2. The cartridges are placed in air-tight metal cans for shipment to the field.

Air samples are collected using a standard high-volume sampler (General Metal Works, model GS2310, Village of Cleves, OH) modified with an aluminum tube behind the filter holder and ahead of the motor (figure 3). The standard motor was replaced with a two-stage Lamb motor (Amtek-Lamb, model 115937, Kent, OH) that maintains a flow rate of 34 cubic meters per hour (m^3/hr) through one XAD cartridge. The samplers have also been fitted with

Figure 3. Schematic of high-volume air sampler for organic compounds

automatic filter covers (Andersen Model GMW-8550, SamplSaver). The air sampling equipment is operated and calibrated according to the manufacturer's recommendations. Flow rates of the high-volume samplers are calibrated quarterly using a standard manometer calibrator (General Metal Works, Village of Cleves, OH). The samplers with resin cartridge vapor traps are set to sample air at a flow rate of 566 liters per minute (L/min) or 20 cubic feet per minute (ft^3/min). A small reference manometer is used as a qualitative check to verify normal operation between calibrations.

Duplicate samples are collected for a 24-hour period (815 m^3) every 12 days. All valid duplicate samples were analyzed. Typically the samplers are set up on a Tuesday and programmed to run sometime during the following week. The exposed filter and cartridge are then picked up the following Tuesday. Because a full-time operator staffs the Point Petre site, samples taken there are usually picked up the day after they are collected. Filters are folded in half with the deposit facing in, wrapped in aluminum foil, and sealed in a plastic bag. Cartridges are placed in metal cans for shipment to the Water Survey laboratory.

Upon receipt at the laboratory, filters are equilibrated at 50 per cent relative humidity for 24 hours and weighed. Three filters taken by the same sampler are selected to make a composite sample. Each filter is wrapped in aluminum foil, and composite sets are sealed in plastic bags and stored at -20EC before extraction and analysis. The XAD-2 in the cartridges is poured into clean glass jars with Teflon-lined caps and stored at -20EC.

2.1.5 Sampling for Trace Metals in Air

Samples of airborne particles are collected on 37-mm TeflonJ filters (R2PJ037, Gelman Sciences, Inc., Ann Arbor, MI) for trace metals analysis by X-ray fluorescence (XRF). These filters are equilibrated for 24 hours at 50 per cent relative humidity before weighing on a six-place microbalance (Model C-31, Cahn Instruments, Cerritos, CA). The filters are then placed in color-coded polypropylene holders and sealed in snap-lock Petrie dishes for shipment to the field sites.

Particle samples are collected using a commercial dichotomous sampler (Anderson Samplers, Atlanta, GA) at the three U.S. IADN stations only. Rather than using a PM-10 inlet, the inlet to the dichotomous sampler is mounted in a standard high-volume sampler shelter so that larger particles can be collected. Particles are separated by a virtual impactor into a fraction of fine < 2.5 micrometers (:m) aerodynamic diameter and a coarse fraction > 2.5 :m aerodynamic diameter. The overall flow rate is set at 1 m^3/hr at the start of each sampling period. Samples are collected for a 96-hour period during each 28-day sampling cycle. Samples were collected over four consecutive days (Friday through Monday). Starting in 1993, the four separate sampling days have been spread throughout the 28-day cycle. For both of these sampling schedules, the entire air sample (about 96 m^3) passes through a single pair of Teflon filters.

Before shipment to the laboratory, the coarse filter is removed from its polypropylene holder and mounted in a special holder (PetrieSlide, Millipore Corp., Bedford, MA) to prevent movement and loss of coarse particles during shipment. Previous work (Sweet et al., 1990) has shown that this step is not necessary for filters with fine particles so they are shipped in their polypropylene holders in the snap-lock Petrie dishes. Upon receipt at the laboratory, the filters are equilibrated for 24 hours at 50 per cent relative humidity and reweighed. The filters are then enclosed in PetrieSlides (both fine and coarse) and shipped to the USEPA Atmospheric Research and Exposure Assessment Laboratory (EPA/AREAL) for trace metal analysis by XRF. In the laboratory, all filter transfer steps are carried out on a laminar-flow clean bench.

2.1.6 Sampling for Total Suspended Particles and Total Carbon

Samples of airborne particles are collected for determination of total suspended particles (TSP) and total carbon using standard methods (ASTM, 1990). Glass fiber filters (Whatmann EPM 2000) are equilibrated for 24 hours at 50 percent relative humidity before weighing. TSP sampling is conducted only at the three U.S. IADN stations. Air is sampled for 24 hours at a flow rate of 68 m^3/hr once every six days using the EPA sampling schedule. When the sixth day falls on a Tuesday, the day for servicing the site, the sample is skipped. The samplers are calibrated as described in section 2.1.3.

After the final weight of the sample is determined in the laboratory, TSP mass is calculated and recorded on the field data sheet (see section 2.3.2). Three circles, each 1.9 mm in diameter, are then removed from the exposed area of the filter using a cork borer. These circles are analyzed for total carbon (the sum of organic, elemental, and carbonate carbon) using a total carbon analyzer (Dohrmann, Santa Clara, CA). This instrument heats the sample to 850EC in a stream of oxygen and measures the CO_2 produced by infrared absorbance. These results are used to calculate total carbon in :g/m^3. All filters are handled in the laboratory on a laminar-flow clean bench. Filter handling in the field is described in section 2.1.3.

2.2 Laboratory Methods

2.2.1 General Laboratory

2.2.1.1 Glassware Cleaning

All glassware is cleaned with Alconox and water, oven dried, and open ends are wrapped in aluminum foil. Glassware is heated to 450EC for 4 hours in a glassware cleaning furnace (Model 210, Wilt Industries, Inc., Lake Pleasant, NY) to eliminate all organic matter. Glassware with tougher stains is rinsed with methanol and dichloromethane before washing. Pipets and volumetric flasks used for standard preparation are soaked in a 50:50 (v:v) sulfuric acid:nitric acid solution overnight before washing. Other supplies (forceps, Teflon liners, stainless steel needles from N_2 blowdown)are cleaned by ultrasonication with dichloromethane.

2.2.1.2 Precleaning

Polyurethane foam, 0.022 g/cm^2(Olympic Products Inc., Greensboro, NC) is cut to the desired size and precleaned by Soxhlet extraction for 48 hours with dichloromethane and 50:50 (v:v) acetone:hexane. The PUF is dried in a heated vacuum desiccator, wrapped with solvent-rinsed aluminum foil, and stored in a sealed can at -20EC until it is shipped to the field station.

The procedure for precleaning XAD-2 is outlined in figure 4. XAD-2 amberlite resin (20-60 mesh, Sigma Chemical Co., St. Louis, MO) is rinsed with water and extracted with a series of pesticide-grade solvents. Each solvent is used for at least 24 hours in the following sequence: methanol, acetone, hexane, methylene chloride, hexane, acetone, and methanol. For vapor cartridges, 50:50 (v:v) acetone:hexane is used instead of methanol as the final solvent. After

Figure 4. Flowchart of XAD-2 Precleaning Procedure

Rinse XAD-2 with DI water to remove fines

Methanol

extract 24 hours

Acetone

extract 24 hours

Hexane

extract 24 hours

CH_2Cl_2

extract 24 hours

Hexane

extract 24 hours

AIR SAMPLES	PRECIPITATION SAMPLES
50% acetone/50% hexane extract 24 hours	Acetone extract 24 hours
Oven dry at 65EC	Methanol extract 24 hours
Store at -20EC in amber bottle	Exchange to Milli-Q water; store at 4EC in amber bottles

Finally, the XAD-2 to oven dried at 65EC and stored in an amber bottle at -20EC. The XAD-2 for precipitation columns is exchanged to "Milli-Q" water for storage.

The glass fiber filters (GFF) were used as received from the manufacturer. Beginning in 1993, the GFF were preconditioned overnight at 450EC.

Reagents and other supplies (sodium sulfate, silica gel, glass wool, and teflon boiling chips) are purchased from commercial sources. They are all cleaned by Soxhlet extraction or by heating in a muffle furnace prior to use. Pesticide-grade solvents (EM Science Omnisolv^{TM}) are free from interfering contaminants and require no additional purification.

2.2.1.3 Safety

Preparation and analysis of IADN samples from all matrices require the use of large volumes of organic solvents and the handling of toxic standards. All experiments are performed in fume hoods with air flow of 80 to 120 linear feet per second to minimize exposure to toxicants. Chemists are required to wear a lab coat, safety glasses, and gloves. The laboratory is equipped with a shower, automatic eye wash, and fire extinguisher.

2.2.2 Sample Preparation

2.2.2.1 Air Sample Extraction

Air vapor samples are collected on polyurethane foam or XAD-2 resin cartridges. Particulate matter is

collected on high-purity glass fiber filters. XAD-2, PUF, and GFF samples received from IADN sites are stored at -20EC until they are extracted. The extraction procedure is outlined in figure 5. On the day of extraction samples are transferred to 500-mL Soxhlet extractors and spiked with surrogate standards: PCB congeners #14, 22.19 nanograms (ng); #65, 4.74 ng; #166, 4.76 ng). They are extracted with 350 mL of 50:50 (v:v) acetone:hexane for 24 hours at approximately 15 minutes per cycle. The extracts are concentrated to about 3 mL by rotary evaporation, and the solvent is exchanged to hexane. The concentrated extracts are chromatographed on columns containing 4 to 8 g of 3 percent deactivated silica gel with a sodium sulfate cap to remove interfering polar compounds. Two fractions are collected. The first fraction, eluted with hexane, contains all PCBs, as well as HCB, DDE, aldrin, and mirex. The second fraction, eluted with 40 percent dichloromethane in hexane, contains all PAHs, "-HCH, (-HCH, dieldrin, "-chlordane, (-chlordane, trans-nonachlor, DDD, and DDT.

2.2.2.2 Precipitation Sample Extraction

Two methods have been used to remove organic compounds from precipitation samples. One method uses extraction disks (Empore C-18, Analytichem, Harbor City, CA), and the other uses XAD-2 columns. Empore disks were used at Pt. Petre before January, 1992 and at Eagle Harbor before September, 1991. Rain samples are spiked with PCB surrogate standards as described in section 2.2.2.1 and vacuum filtered through 47-mm extraction disks. Analytes are eluted by washing with hexane and dichloromethane. Samples are concentrated by rotary evaporation and chromatographed on a 4-g, 3 percent deactivated silica column. Two fractions (hexane and 40 percent dichloromethane in hexane) are collected.

Figure 5. Flowcharts for Air Sample Extraction: Procedure for GFF and XAD-2 Cartridges

Setting up Extraction:

350 mL of acetone/hexane (50:50) in 500 mL round-bottom flask with boiling chips

Put sample in Soxhlet with rinse

Spike sample with 100 ：L PCB surrogate

standard

Turn on heater

Turn on condenser water

Cover Soxhlet and flask with foil

Extract for 24 hours

Taking down extraction:

Turn off heater

After 2 hour, turn off water

Siphon off as much solvent as possible

Stopper flask and store in cool dark place

In the second method, standard glass chromatographic columns (30 x 2 cm) are packed with about 7 g (10 cm) of wet XAD-2 held in place by glass wool plugs. The column contents are Soxhlet extracted with 50:50 (v:v) acetone:hexane for 30 hours. The procedure is outlined in figure 6. Samples are concentrated by rotary evaporation. The water layer is removed and back-extracted with hexane three times in a separatory funnel. All extracts are combined, concentrated, and chromatographed on a 4-g, 3 percent deactivated silica column with a 1.5-inch sodium sulfate cap to absorb residual water. The procedure for the silica column separation is outlined in figure 7.

2.2.2.3 Sample Concentration and Transfer

Each fraction is then concentrated by rotary evaporation, transferred to 4-mL amber vials, and stored at -20EC. The 40 percent dichloromethane fraction is solvent-exchanged to hexane.

2.2.2.4 Nitrogen Blowdown

Samples are further concentrated under a slow stream of ultra-pure nitrogen in a heated evaporating unit to between 0.4 and 2.0 mL depending on the sample site, matrix, and season, as shown in table 1.

2.2.2.5 Internal Standard and Autosampler Microvial Preparation

Internal standards (ISTD) are added to all samples prior to gas chromatographic (GC) analysis. Details are given in table 2. For analysis of PCBs and pesticides in the hexane fraction, the internal standards are 8 ng and 6 ng of PCB congener #30 and #204, respectively. For

Figure 6. Flowchart for the Extraction of Rain Samples

Rain on XAD-2 in Soxhlet

Assemble Soxhlet and flask

Add 150 mL acetone on XAD-2 in Soxhlet

Add 150 mL hexane on XAD-2 in Soxhlet

Spike with 100 ：L PCB surrogate

Turn on heater and condenser water

Hand-induce siphoning for the initial three to four flushes

Extract for 30 hours

Figure 7. Procedure for Silica Column Chromatography Separation

3% deactivated silica

Silica slurry in hexane

3.5" column (GFF and rain)

7" column for air XAD-2

Top column with $NaSO_4$

Equilibrate column with hexane

Load sample

Elute with hexane: 1st fraction contains PCBs, DDE, HCB, aldrin, and mirex

25 mL for GFF, 30 mL for rain

50 mL for XAD-2

Collect eluent in pear-shaped flask

Add switching volume: 4 mL for GFF, 5 mL for rain, and 8 ml for XAD-2

Collect in same flask

Change flask

Elute with 40% CH_2Cl_2 in hexane:	2nd fraction contains
25 mL for GFF	"-and (-HCH, dieldrin, DDD, DDT, "-chlordane, (-chlordane, t-nonachlor, and all PAHs
30 mL for rain	
50 mL for XAD-2	

Table 1. Approximate Final Sample Volumes after N_2 Blowdown

Type of sample		*Approximate volume after N_2 blowdown (mL)*	
		Hexane fraction	*40% fraction, pesticides*
Rain	Winter	0.4	0.4
	Summer	0.4	0.4
GFF	Winter	0.4	0.4
	Summer	0.4	0.8
XAD-2	Winter	0.4-0.8	1.0-2.0
	Summer	0.8-1.0	1.5-2.0

Table 2. Details of Internal Standard Spikes

Fraction	*Compound*	Type of sample	Internal standard	Spike volume (:L)	*Final mass in sample (ng)*	*Color of dot on label*
Hexane	PCBs and pesticides	Vapor, particle, and rain	PCB 30	100	8	Red
			PCB 204		6	
40	PAHs	Vapor, particle, and rain	Anthracene, -d_{10}	50	200	Black
			Benzo(") anthracene -d_{12}		200	
			Triphenylmethane		100	
40%	Pesticides	Vapor	PCB 65	100	23.7	Blue
		Particle	PCB 65	100	4.74	
		Rain	PCB 65	100	4.74	

Note: 40 percent fraction for PAH analysis should be spiked after pesticide analysis is done.

pesticides present in the 40 percent dichloromethane fraction, PCB congener #65 is used as the internal standard. After pesticide analysis is completed on the 40 percent fraction, anthracene-d_{10}, triphenylmethane, and benzo(")anthracene-d_{12} are added as internal standards for the PAH analysis. For GC analysis, approximately 200 :L of spiked sample is transferred to an autosampler vial which is capped tightly.

2.2.3 Standards

This section describes how standards used in the analytical work are prepared.

2.2.3.1 Sources

Standards are prepared from reference materials available from USEPA Environmental Monitoring Systems Laboratory (EMSL), Cincinnati, OH, or from commercial sources. The source, lot number, identification, and purity of each reference material are recorded. Each reference standard is diluted with

hexane (preferred) or an appropriate solvent to prepare a stock standard. Stock standards are further diluted, and composite working standards are prepared for daily use.

2.2.3.2 PCB Standards

Calibration Standard

Aroclors 1232, 1248, and 1262 are mixed in the proportion of 25:18:18 to obtain a total concentration of 610 ng/mL (as described by Mullin, 1985). PCB congeners #14 (22.19 ng/mL), #30 (8 ng/mL), #65 (4.74 ng/mL), #166(4.76 ng/mL) and #204(6.0 ng/mL) are added as surrogate recovery standards and quantitative internal standards.

Surrogate Recovery Standard

PCB congeners #14, #65, #166 are diluted in hexane to achieve concentrations of 221 ng/mL, 47.4 ng/mL and 47.6 ng/mL respectively. Each sample is spiked with 100 ：L of this standard prior to extraction.

610 Recovery Standard

This standard is utilized for matrix spike experiments and to calculate the recovery of individual PCB congeners. The composition of this standard is the same as the calibration standard, but no internal standards are added.

Internal Standard

The ISTD solution is prepared with PCB congeners #30 (80 ng/mL) and #204 (60 ng/mL). 100 ：L of this is used to spike each sample prior to GC analysis.

2.2.3.3 Pesticide Standards

Pesticides elute in two fractions and require two calibration standards.

Calibration Standards

Hexane fraction: Individual pesticides are combined to achieve individual concentration levels of 20 ng/mL. PCB congeners #30 and #204 are added as internal standards.

40 percent dichloromethane fraction: Individual pesticides were combined to achieve individual concentration levels of 20 ng/mL. PCB congener #65 was added as the internal standard. Congener #30 was omitted from this standard as it coeluted with (-HCH.

Recovery Standard

A mixture of all pesticides (100 ng/mL) was prepared in hexane. No ISTD was added. This standard was used for matrix spike experiments to calculate the recovery of each analyte.

Internal Standard

PCB congener #65 was used as the ISTD for pesticide analysis of 40 percent dichloromethane in hexane fractions. A low standard (47.4 ng/mL) and a high standard (237 ng/mL) were prepared to spike precipitation samples and vapor samples, respectively.

2.2.3.4 PAH Standards

Calibration Standard

PAHs are combined to achieve individual concentration levels of 2 :g/mL. This standard is further diluted with hexane to achieve working standards in the range of 0.05 to 2.0 :g/mL. Three ISTDs are added (anthracene-d_{10}, triphenylmethane, and benzo(")anthracene-d_{12}).

Recovery Standard

PAHs are combined to achieve a mixed PAH standard (2 :g/mL) in hexane. This standard is used to determine individual analyte recovery for matrix spike experiments.

Internal Standard

An ISTD solution contains anthracene-d_{10}, triphenylmethane, and benzo(")anthracene -d_{12} at 4.0, 2.0, and 4.0 :g/mL, respectively, in hexane. A 50-:L quantity of this solution is added to each 40 percent dichloromethane extract prior to GC/MS mass spectrometer analysis to achieve final levels of 0.2, 0.1, and 0.2 :g/mL, respectively.

Calibration standards, recovery standards, and internal standards are replaced yearly. New standards are compared with old standards prior to use. All standards are stored in amber bottles, sealed with TeflonJ tape, and stored at -20EC.

2.2.4 Gas Chromatography with an Electron Capture Detector (ECD)

2.2.4.1 System Description

PCBs and organochlorine pesticides are analyzed on a Hewlett Packard (HP) 5890A gas chromatograph with an electron capture detector (Ni-63). Sample injections are controlled by an HP 7673 autosampler. Chromatographic separation is done on a 30-m, DB-5 capillary column, 0.25-mm i.d., 0.25-:m film thickness (J.W. Scientific, Folsom, CA). Hydrogen is used as the carrier gas, and 5 percent methane in argon is used as the detector make-up gas. Instrument operation and data reduction are controlled with a Hewlett Packard 3365 Chem-Station^{TM}.

2.2.4.2 Analytical Program

Chromatographic conditions were optimized to achieve 50 percent resolution between PCB congeners #17 and #18. Typical conditions are:

Injector temperature: 250EC

Detector temperature: 350EC

Purge vent: 2 mL/minute at 70EC

Total ECD flow: 22 mL/minute

Split vent: 130 mL/minute

Injection volume: 1 :L

PCB conditions: 260.33-minute oven program

Initial temperature: 70EC, hold 1 minute

Ramp 1: 5EC/minute to 140EC

Ramp 2: 0.3EC/minute to 210EC

Ramp 3: 10EC/minute to 280EC hold 5 minute

Pesticide conditions: 147-minute oven program

same as PCB program except as follows:

Ramp 2: 0.2EC/minute to 160EC

final hold: 20 minute

2.2.4.3 Instrument Operation and Calibration

A hexane blank, an appropriate calibration standard, and all samples from one extraction set are loaded onto an autosampler. A sample log sequence is made with the HP 3365 Chem- Station^{TM}. The sequence ends with a hexane blank and a standard. One ：L of sample is injected into the GC.

A hexane blank is run to ensure that the system is free from interfering peaks. The calibration standard is assayed to evaluate system performance and to calibrate the instrument. Corrective action is taken if the chromatography does not meet performance criteria.

For PCB analysis, the 610 calibration standard (see 2.2.3.2) is used to calibrate the GC. Individual PCB congeners in the calibration standard are identified from Mullin's (1985) chromatogram. The baseline of each peak is corrected, and the area is integrated with a 3365 Chem-Station^{TM}. Integration events are saved and a calibration table is created with the retention time, amount, and response factor for each congener.

For pesticide analysis, two pesticide calibration standards (see 2.2.3.3) are used. Peaks are identified by matching the retention time obtained when each compound is injected separately. After baseline correction and peak area integration, two calibration tables are generated with the retention time, amount, and response factor for each pesticide.

2.2.4.4 PCB Data Reduction

In a sample chromatogram, PCB congeners are identified, integrated after proper baseline correction, and quantitated from the calibration table using the internal standard procedure. Congener #30 is used for the first half of the chromatogram, and #204 is used for the second half. All integration events are saved. A congener-specific internal standard quantitation report and a text file are created for each sample. The sample text file is imported to a Lotus 1-2-3 file for computation of total PCBs and surrogate recoveries.

2.2.4.5 Pesticide Data Reduction in the Hexane Fraction

From the PCB chromatogram, hexachlorobenzene, aldrin, DDE, and mirex are identified and quantified as described above for PCBs. The GC is calibrated with a pesticide standard (see 2.2.4.3). PCB congener #30 is used as the internal standard for all pesticides except mirex. PCB congener #204 is used for mirex quantitation.

2.2.4.6 Pesticides in the 40 Percent Dichloromethane Fraction

"-HCH, (-HCH, dieldrin, a-chlordane, (-chlordane, trans-nonachlor, DDD, and DDT are obtained from the 40 percent fraction. A calibration table is created for a pesticide standard (see 2.2.4.3). PCB congener #65 is used as the internal standard. Peak identification, baseline correction, and quantitation are done in the same way as for PCBs. An internal standard quantitation report, integration events, and a text file are created for each sample.

2.2.5 Gas Chromatography with a Mass Selective Detector (MSD)

2.2.5.1 System Description

PAH analyses are performed on a Hewlett-Packard 5890 gas chromatograph with a 5970A Mass Selective Detector (MSD), a 59970 MS ChemStationJ, and a 7673 autosampler. Chromatographic resolution is achieved with a 30-m, DB-5, 0.25-mm, 0.25-:m, capillary column (J & W Scientific, Folsom, CA) with helium carrier gas. The selected ion monitoring (SIM) mode is utilized. The PAH compounds measured are listed in table 3.

2.2.5.2 Method Description

PAHs are determined by capillary GC with a mass-selective detector (GC-MSD), SIM mode, using the method of internal standards. A lab blank and a matrix spike are included with each sample set. Matrix spikes are utilized to determine the recovery of each analyte.

2.2.5.3 Instrument Set-up and Performance Evaluation

The oven temperature program is optimized to achieve greater than 50 percent resolution for the following peaks:

amu=252: benzo(b)fluoranthene and benzo(k)anthracene

amu=228: chrysene and benzo(")anthracene

Table 3. PAH Compounds Measured

Peak #	*Analyte*	*Major ion*
1	Napthalene	128
2	Acenapthylene	152
3	Acenapthene	153
4	Fluorene	166
5	Phenanthrene	178
6 (ISTD#1)	Anthracene-d_{10}	188
7	Anthracene	178
8 (ISTD#2)	Triphenylmethane	244
9	Fluoranthene	202
10	Pyrene	202
11	Retene	219
12 (ISTD#3)	Benzo(a)anthracene-d_{12}	240
13	Benzo(a)anthracene	228
14	Chrysene	228
15	Benzo(b)fluoranthene	252
16	Benzo(k)fluoranthene	252
17	Benzo(e)pyrene	252
18	Benzo(a)pyrene	252
19	Indeno(123cd)pyrene	276
20	Dibenzo(ah)anthracene	278.1
21	Benzo(ghi)perylene	276
22	Coronene	300.3

In addition, the temperature program is adjusted to obtain greater than 50 percent resolution for any known interfering peaks present in the samples. Typical conditions are as follows:

Injector (splitless): 275EC

Transfer line: 300EC

Purge vent: 3.8 mL/minute at 40EC

Column linear velocity: 33 cm/second (helium)

Split vent: 16.9 mL/minute

Injection volume: 1 :L

Oven program: 68-minute oven program

Initial Temperature: 40EC, hold 1 minute

Ramp 1: 25EC/minute to 140EC

Ramp 2: 4EC/minute. to 240EC,

Ramp 3: 2EC/minute to 290EC, hold 13 minutes

At the beginning of each run, the GC-MSD system performance and calibration are verified for all analytes. The mass spectrometer is tuned immediately prior to each run using the system operating software (autotune and manual tune) programs with perfluorotributylamine (PFTBA) calibration gas. MSD controls are adjusted so that masses 69, 219, and 502 and their respective isotopes meet the target mass-intensity criteria. Hexane is injected immediately prior to each run to ensure that the system is free from contaminants or interfering peaks. Records of daily system performance and maintenance are kept.

2.2.5.4 System Calibration

A multipoint calibration report is prepared for each analyte at the beginning of every sample batch. Calibration standards are injected approximately every seven samples and at the end of each run. The system is recalibrated if a shift in instrument response is observed. The internal standard calibration procedure is utilized with three internal standards. Two deuterated PAHs (anthracene-d_{10} and benzo(")anthracene-d_{12}) and triphenylmethane are used for internal standards. The chromatogram is divided into three time segments, and each segment is calibrated relative to the response of one internal standard.

2.2.5.5 Sample Analysis

PAH analyses are performed on the 40 percent dichloromethane in hexane fraction after pesticide analyses have been completed. Samples are stored in amber vials at -20EC until GC/MSD analysis is performed. Samples are equilibrated to ambient temperature, and three internal standards are added (anthracene-d_{10}, triphenylmethane, and benzo(")anthracene-d_{12}) immediately prior to analysis.

One-:L samples are injected using an autosampler. A sample log is completed for each sample set assayed.

2.2.5.6 PAH Data Reduction

An individual data file, a hard copy internal standard report, and a chromatogram are created for each sample injected. Calibration reports are stored with each run. The chromatograms and reports are reviewed by the analyst to ensure that each analyte is properly identified (i.e., that mass and retention time match with standards) and that peaks are integrated correctly. Corrective action is taken as needed, and the action is documented on the report. The area counts and the quantitative results for each analyte are manually entered into spreadsheet files for further processing. All data entries are reviewed twice prior to submission to the principal investigator (PI).

2.3 Data Management

2.3.1 Meteorological Data

Meteorological data are automatically transferred to cassette tapes, which are mailed to the ISWS every two weeks. Recently the Eagle Harbor (starting January 1, 1993) and Sleeping Bear (starting August 1, 1992) sites were equipped with telephone lines and modems. Currently data from these two sites are accessed daily by phone. The meteorological data from Point Petre are collected by Environment Canada and provided annually to the ISWS.

Hourly average values for temperature, wind speed and direction, precipitation, solar radiation, and relative humidity are scanned by computer for missing data, out-of-range data, unusual rates of change (e.g. >10EF per hour), or unusually uniform values (e.g., the same average wind speed for 12 or more consecutive hours). Problems are examined manually; if there seems to be a problem with the sensor, the data are flagged or deleted. In a few cases, blocks of missing data at Eagle Harbor were replaced by data collected at the Houghton airport (42 km SW of the site).

2.3.2 Field Sampling Data

All site operators use the same written protocols for sampling operations; and at each site, a log is maintained describing activities carried out during all site visits. Every sample collected is assigned a unique identification code, and all information associated with the sample is entered on a field data sheet. Copies of the sampling protocols and the field data sheet are given in appendix A. The identification code begins with a single-letter site identifier. This is followed by letter codes indicating the sample type (precipitation, high-volume air, etc.) and the date sampling was completed in a year-month-day format. The code identifies the sample throughout laboratory analysis and data reporting.

When analytical data are received, the sample volume and other pertinent information are entered into a spreadsheet (see section 2.3.4). At this time, the data are examined for problems and flagged if necessary. Files containing original data sheets and all sampling records are maintained at the Water Survey.

2.3.3 Chromatography Data Generation

Final chromatography data for PCBs and PAHs (sections 2.2.4. and 2.2.5.) are transferred to a spreadsheet and given to the PI. Hard-copy reports of the pesticide data are also given to the PI.

2.3.4 Spreadsheet Construction

Analytical data from the chromatography spreadsheets and sampling data from the field data sheets are combined in a data spreadsheet as the analytical data are received from the laboratory. The sample identifying code, sample volume, and other pertinent information are entered from the original field data sheet. The chemical data are entered electronically in the same row from the PCB and PAH chromatography spreadsheets. Pesticide data are added by hand from the data reports. For each sample entry (row) in the spreadsheet, any problems are noted and some concentration values and PCB homolog distributions are calculated. Although a number of quality assurance (QA) parameters are included in the chemical data spreadsheet, complete QA data are maintained in a separate spreadsheet. The chemical data spreadsheet is used to prepare monthly reports (section 2.3.5) and the official chemical database for the project (section 2.3.6).

2.3.5 Monthly Reports

Monthly reports of samples collected and undergoing laboratory analysis are compiled and distributed to the USEPA and the site coordinators. This report also includes cumulative chemical data summaries for all of the analytes at all of the sites. These summaries are prepared from the data spreadsheets and are revised each month to include all of the data generated in the network. An example of a monthly report is included in appendix A. Every two months, a summary of all sampling information collected by the site operators is prepared from the original data sheets and distributed as above.

2.3.6 Database Construction

Using R-Base software (Microrim, Redmond, WA), a database has been constructed to facilitate the processing of information on all analytes (PCBs, pesticides, and PAHs). This database consists of one primary data table plus additional auxiliary tables. The primary data table includes analysis results for all analytes at all IADN sites, plus other necessary information, such as volumes and sampling dates. The auxiliary tables are only needed to automate the procedures (one main program and three subprograms) that generate the summary tables, and do not contain analytical data. The database also includes PCB, PAH, and pesticide QA tables, and a table of field blank information.

Conversion to the appropriate units and the handling of blanks are done in the database prior to processing. For all analytes, the limit of detection (LOD) and method detection limit (MDL) are tabulated for comparison to the analytical data. Section 3.3.3 (p. 65) explains how these terms are calculated.

2.4 Statistics and Explanation of Results Tables

This section is included to provide definitions and explanations of the data that appear in the tabulated results for both air and precipitation samples (section 3 of this report). A number of quantities, including the arithmetic mean, standard error of the mean, and percentiles of the observed distribution, are common to the tables for both types of samples. The geometric mean and geometric standard deviation appear only in the tables of measured concentrations in air, while the precipitation-weighted mean and the standard error of a precipitation-weighted mean are used only in the tables of precipitation sample results. Obviously, these tables are the only ones that contain information on precipitation amounts and several other quantities related to precipitation. Total PCBs, average values, and other statistics are calculated using the actual results even if the value is below the nominal LOD or IDL for a particular analyte. When no peak was found, a value of "0" is used.

Tables for both air and precipitation include information on the expected number of samples,

the number actually analyzed, and the number having measured concentrations less than the LOD. The expected number of samples is the number that should have been collected during the given seasonal or annual period, assuming that the sampling schedule was followed exactly and no samples were lost. The actual number of samples and the number <LOD are self-explanatory.

The well-known arithmetic mean, x^C, is defined as:

where x_i is the measured concentration in an individual sample i, and n is the total number of analyses. Concentrations are determined by dividing the analyte mass by the measured sample volume. Air volumes are corrected to equivalent volumes at 20EC and 1 atmosphere pressure. The percentile values were computed using the method given by Cleveland (1985). The median is taken to be the 50th percentile value.

The geometric mean and geometric standard deviation are used only in the tables of concentrations in air. The geometric mean, x^C_g, is defined as:

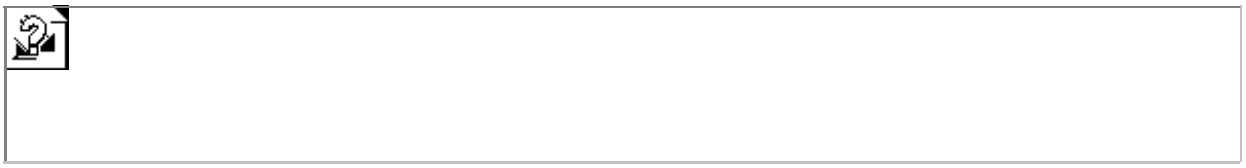

where exp is the exponential function and ln is the natural logarithm.

The geometric standard deviation, S_g, is defined as:

The precipitation-weighted mean concentration, x^C_w is given by:


where P_i = precipitation amount for sample i.

Endlich *et al.* (1988) expressed the standard error of a weighted mean, SEM_w, as an approximate ratio variance, as given by Cochran (1977). The formula that follows is given in an SRI International (1986) report:


where P is the mean precipit amount for samples l ... n.

Several data columns in the tables of concentration in precipitation provide information that could be used for completeness criteria (i.e. expected, actual, and <LOD). The third column gives the percentage of time that the raingauge was operational, so one may judge whether the reported precipitation amount is meaningful. The next column gives the precipitation amount measured by the raingauge The eighth column gives the percentage of the *measured precipitation* during the period represented by the analyzed samples. In some cases this is >100 percent. This may be caused by the raingauge being out of operation during a portion of the sampling period. It can also occur when a 4-week sample overlaps two seasons (e.g. an August 18 to September 13 sampling period overlaps summer and fall). The sample is counted as a fall sample, but the rain occurring in late August is part of the summer total. Finally, the ninth column

gives the percentage of the sampler catch efficiency, which is the sample volume divided by the volume equivalent of the Belfort precipitation amount for those samples.

All of the values in the data tables are based on actual values that were not corrected for blanks or recoveries. Average analytical recoveries are given in Appendix B and in the quality assurance report (Harlin *et al.*, 1994). The LOD and MDL are given for each analyte in each matrix in the data tables. The values are adjusted for the average sample volume (vapor = 815 m^3; particles = 2450 m^3; precipitation = 10 L) to give LOD and MDL values in pg/m^3 or ng/L. In some cases when the volume for a particular sample is above the average volume, an analyte may be above the LOD; but the concentration may be below the volume adjusted LOD value in the tables.

3. RESULTS

3.1 Meteorological Measurements

3.1.1 Database Configuration

Meteorological data are maintained in a fixed-field R-Base database on a personal computer. The fixed fields include Julian date, time, year, station ID, temperature, relative humidity, solar radiation, wind speed, wind direction, and precipitation amount. Data are available as hourly averages. A complete meteorological database is available on disk.

3.1.2 Meteorological Summary

A tabulated summary of meteorological data is presented for each of the three IADN sites (table 4). The project data period incorporates the period from individual site start-up to 31 December 1992. *Data periods vary between sites and do not correspond to a calendar year*. The seasons are based on the meteorological year (winter: December, January, February; spring: March, April, May; summer: June, July, August; fall: September, October, November) and may not always include the entire data period. The meteorological data were recorded at the respective field sites, with the exception of a three-month period (13 November 1990 to 6 February 1991) at Eagle Harbor. Meteorological data from the airport at Houghton, MI (25 miles from the field site) were used in place of the missing data.

A number of meteorological parameters are provided in table 4. Average temperature refers to the average of all hourly values, average maximum and average minimum temperatures refer to the average of the daily extremes, and highest and lowest temperatures refer to

Table 4. Site Meteorological Summary

Season	Temperature (^oC)					Precipitation (cm)			Avg daily solar (MJ/m^2)	Avg wind speed (kph)	Avg R.H. (%)
	Avg	Avg max	High	Avg min	Low	Total	Rain	Snow			
Eagle Harbor (13 November 1990 to 31 December 1992)											
Winter	-6	-2	8	-9	-22	28.4	4.2	24.2	2.59	12.6	83
Spring	4	8	27	0	-18	31.5	28.5	3.0	16.02	11.1	78
Summer	16	20	32	11	0	19.5	19.5	0.0	20.21	8.8	82
Fall	6	8	26	3	-12	48.2	41.4	6.8	6.90	13.0	85
Study period	5	8	32	1	-22	128.	93.6	34.0	12.72	11.4	82
Sleeping Bear Dunes (12 December 1991 to 31 December 1992)											
Winter	-2	0	11	-4	-16	26.3	10.6	15.7	3.43	11.9	86
Spring	5	9	27	0	-11	15.8	11.3	4.5	16.32	10.3	75
Summer	16	21	30	11	0	13.9	13.9	0.0	20.75	8.4	79
Fall	8	11	27	5	-7	35.2	33.0	2.2	7.91	10.9	81
Study period	6	10	30	2	-16	91.2	68.8	22.4	11.67	10.5	80
Sturgeon Point (14 November 1991 to 31 December 1992)											
Winter	0	3	16	-3	-20	26.8	20.8	6.0	4.98	13.2	86
Spring	5	10	32	1	-17	22.8	16.0	6.8	20.92	10.5	85
Summer	18	22	31	13	5	43.3	43.3	0.0	26.74	8.5	87
Fall	10	13	26	6	-6	32.3	31.0	1.3	11.17	11.7	84
Study period	7	11	32	3	-20	125.	111.1	14.1	15.02	11.3	86

extremes recorded for a single hour. Total precipitation is measured in a weighing bucket raingauge with a Nipher wind shield, but snow events are not recorded directly in the database. Precipitation attributed to snow was calculated, and snow was assumed to occur with temperatures $\leq$ 0EC and rain with temperatures > 0EC. Average daily solar radiation (megajoules per square meter, MJ/m^2) was calculated as the average sum of a 24-hour period (midnight to midnight). Average wind speed (kilometers per hour,

kph) and average relative humidity (percent) were calculated as an average of all hourly values. All meteorological values are stored in the database in English units and were converted to metric units for this report.

3.1.3 Wind Direction and Wind Speed

Wind roses are presented for each of the three sites for the individual site data periods and for the individual seasons. The wind roses are divided into eight wind sectors and into six wind speed categories. The wind roses for Eagle Harbor (figure 8) show no dominant wind sector; however, dominant wind speeds ranged between 3 and 15 kilometers per hour (kph) with the higher wind speeds commonly associated with the westerly and southerly winds. The winter season shows the greatest variability for wind direction, with winds from the west dominating (63.5 percent). For Sleeping Bear Dunes (figure 9) showed no dominant wind sector and only slight variations with individual seasons. Sturgeon Point (figure 10) also showed no dominant wind sector, although westerly winds dominate (33.1 percent) in the winter, while winds from the south-southeast dominate (20.5 percent) in the fall.

Figure 8. Wind roses for Eagle Harbor for the study period (13 November 1990 to 31 December 1992) and specific seasons

Figure 9. Wind roses for Sleeping Bear Dunes for the study period (12 December 1991 to 31 December 1992) and specific seasons

Figure 10. Wind roses for Sturgeon Point for the study period (14 November 1991 to 31 December 1992) and specific seasons

3.1.4 Precipitation

The largest precipitation amount for the three sites was recorded at Eagle Harbor (128 cm), although this value is a total for a nearly two-year period. Sturgeon Point and Sleeping Bear Dunes recorded 125 cm and 91 cm, respectively, for a nearly one-year period. In precipitation chemistry it is sometimes important to describe the characteristics of the precipitation. As examples, the concentrations of many pollutants in collected precipitation follow an exponential decline with increasing precipitation volume, and there is a possibility that snow removes some atmospheric pollutants more thoroughly than rain. During the sampling period the frequency of light hourly precipitation ($\leq$ 0.3 cm) was greatest in the winter, while the frequency of heavy hourly precipitation ($\geq$ 0.7 cm) was greatest in the summer. This pattern is characteristic of the more frequent localized convective storms occurring during the summer season. The IADN instruments do not directly measure snowfall. However, using temperature as a surrogate -- snow assumed with temperatures $\leq$ 0EC and rain with temperatures > 0EC -- a distinction between rain and snow (precipitation equivalent) can be calculated. Using this assumption, 36, 33, and 12 percent of the precipitation fell as snow at Eagle Harbor, Sleeping Bear Dunes, and Sturgeon Point, respectively.

It is also important to examine the distribution of wind direction during precipitation, to identify a possible impact of local pollutant sources, or to distinguish between onshore and offshore influences. To do this, hourly precipitation amounts were combined with hourly wind directions to create precipitation roses (figures 11 - 13). No attempt was made to **Figure 11. Precipitation roses for Eagle Harbor for**

the study period (13 November 1990 to 31 December 1992) and specific seasons

Figure 12. Precipitation roses for Sleeping Bear Dunes for the study period (12 December 1991 to 31 December 1992) and specific seasons

Figure 13. Precipitation roses for Sturgeon Point for the study period (14 November 1991 to 31 December 1992) and specific seasons

correlate precipitation intensity with wind direction. The precipitation roses are divided into eight wind sectors. The interpretation of the precipitation roses should be limited to local conditions; they *do not* necessarily indicate the movement of storm systems or the long-range transport of pollutants.

The precipitation roses for Eagle Harbor best illustrate the information provided by these calculations (figure 11). The precipitation rose for the entire study period shows considerable variability by wind sector, but the greatest percentage of hourly precipitation events occurred with surface winds from the northwest (onshore winds) and from the east and southeast (offshore winds). The apparent variability in wind sectors can better be resolved by examining the individual seasons. For the winter, the majority (54 percent) of the precipitation events were associated with northwest winds (onshore winds), but the dominant wind sectors shifted to the east (41.1 percent) in the spring and to the south (75 percent) in the summer. The fall season exhibited a more poorly defined pattern, but one dominated by the easterly wind sectors (45.9 percent). Precipitation roses for Sleeping Bear Dunes and Sturgeon Point also show seasonal variabilities (figures 12 and 13).

3.2 Samples Collected and Analyzed

Table 5 lists the numbers of samples collected at the four IADN sites covered in this report between 15 November 1990 and 30 April 1993 and the number of samples analyzed as of 16 May 1993. At Point Petre, this includes analyses of PCBs and pesticides in samples collected between October 1990 and November 1992,and PAH analyses for the period October 1990 to May 1992. Eagle Harbor analyses of PCBs and pesticides cover the period November 1990 to November 1992, and analyses of PAHs cover the period between November 1990 and May 1992. Analyses of PCBs and pesticides for Sturgeon Point and Sleeping Bear cover the period December 1991 to October 1992, and PAH analyses cover the period December 1991 to May 1992. Metals analyses at Eagle Harbor, Sleeping Bear, and Sturgeon Point are for 1992.

Table 5. Samples Analyzed

*Sample type**	*Weeks in operation*	*Total collected*	*Samples analyzed*			
			PCBs	*Pest*	*PAHs*	*Metals*
Eagle Harbor						
Precipitation (organics)	127	32	24	26	17	-
Air vapor	127	69	52	54	39	-
Air particles	127	25	20	21	18	-
Dichot	90	20	-	-	-	14
Sleeping Bear						
Precipitation (organics)	71	16	8	9	3	-
Air vapor	71	40	20	28	6	-
Air particles	71	13	7	7	2	-
Dichot	71	17	-	-	-	9
Sturgeon Point						
Precipitation (organics)	75	17	8	8	3	-
Air vapor	75	39	21	28	9	-
Air particles	75	12	7	7	2	-
Dichot	75	17	-	-	-	13
Point Petre						
Precipitation (organics)	118	29	22	23	14	-
Air Vapor	118	64	48	51	27	-
Air Particles	118	21	15	16	12	-

Notes: *Precipitation samples for organics are collected once every 28 days: Air vapor samples are collected once every 12 days: Air particle samples are monthly composites of three filters: Dichot samples for metals are collected every 28 days.

3.3 Chemical Measurements

3.3.1 Metals

The average concentrations of selected airborne trace metals are given in table 6. For Eagle Harbor and Sturgeon Point, the averages reflect annual averages for 1992 (thirteen 96-hour samples, each covering a 28-day period). At Sleeping Bear, the dichotomous sampler was not operational for four sampling periods during 1992. Detection limits are twice the average standard error provided with the XRF analytical data. Field blank values were obtained from the analysis of filters that had been loaded into the

sampler for the same length of time as sample filters but without any air flow. All field blank values were below the detection limits. The "fine" fraction contains particles whose average aerodynamic diameters are below 2.5 ：m, and the "coarse" fraction contains particles whose average aerodynamic diameters are above 2.5 ：m. Except for Cd, sample values were generally above detection limits for at least one of the size fractions.

3.3.2 TSP/TOC

Average total suspended particles and total organic and elemental carbon (TOC) are given in table 7. At the three U.S. IADN sites, separate samples were collected once every six days for these determinations. At Point Petre only, TSP was measured on the high-volume organic samples, which were collected every 12 days. Figures 14 to 17 present time series for TSP and TOC at the four sites.

Table 6. Average Concentrations of Airborne Trace Metals (ng/m^3)

Element	*Detection limit*	*Eagle Harbor (n=14)*	*Sturgeon Point (n=13)*	*Sleeping Bear (n=9)*
Vanadium				
fine	0.4	0.4	1.2	<0.4
coarse	0.4	<0.4	0.5	<0.4
Chromium				
fine	0.2	0.4	0.6	0.2
coarse	0.4	1.2	1.9	0.6
Manganese				
fine	0.3	1.0	1.8	1.7
coarse	0.6	2.5	2.2	1.8
Nickel				
fine	0.3	0.6	0.9	<0.3
coarse	0.3	0.7	1.2	<0.3
Copper				
fine	0.4	2.9	1.9	1.3
coarse	0.5	5.2	8.4	0.6
Zinc				
fine	1.5	12.0	13.9	7.5
coarse	1.5	1.2	11.4	1.5
Arsenic				
fine	0.3	0.8	0.9	0.5

coarse	0.2	<0.2	<0.2	<0.2
Selenium				
fine	0.2	0.3	1.4	0.8
coarse	0.1	<0.1	<0.1	<0.1
Cadmium				
fine	0.5	<0.5	<0.5	<0.5
coarse	0.5	<0.5	<0.5	<0.5
Lead				
fine	1.1	2.3	8.3	4.4
coarse	0.4	0.4	1.0	0.6

Table 7. Average TSP and TOC Concentration in Air (: g/m^3 " standard deviation)

Site	*N*	*TSP*	*TOC*
Point Petre	54	15.3 " 11.6	-
Eagle Harbor	95	15.0 " 14.3	1.7 " 2.0
Sturgeon Point	55	19.4 " 7.4	2.5 " 1.5
Sleeping Bear	54	14.6 " 10.3	1.8 " 1.3

Figure 14. Time series of TSP and TOC data at Eagle Harbor

Figure 15. Time series of TSP and TOC data at Sleeping Bear Dunes

Figure 16. Time series of TSP and TOC data at Sturgeon Point

Figure 17. Time series of TSP data at Point Petre

3.3.3 Organic Compounds

Tables 8 to 11 list data for total PCBs and 34 selected PCB congeners, 7 pesticides and pesticide metabolites, and 15 PAHs. A total of 29 PCB congeners and coeluting congener groups are reported. These PCBs account for about 90 percent of the mass of PCBs in most samples. The numbers for total PCBs listed in the tables are calculated from the sum of the masses of all detectable PCB congeners (50 to 90 PCBs in most samples). Data are given for organic compound concentrations in three media: airborne vapor, airborne particles, and precipitation. For calculation of seasonal averages, sample data are divided into winter (December, January, February), spring (March, April, May), summer (June, July, August), and fall (September, October, November) based on the day sampling ended. Concentration units are pg/m^3 for air samples and ng/L for precipitation samples.

Limit of detection (LOD) and estimated method detection limit (MDL) values are also given for each analyte. To calculate the LOD, the mean of at least 10 field blanks plus three times its standard deviation is divided by the volume of a typical sample (815 m^3 for vapor, 2450 m^3 for particles, and 10 L for precipitation). This value is the maximum probable contribution of the field blank to the concentration reported in the samples. The MDL is estimated from the instrument detection limit (IDL). The IDL is determined by injecting "low-level" standard solutions into the chromatograph. The concentration of the analytes in these solutions is selected to yield a chromatographic response with a signal to noise ratio of 3 to 5. The IDL is calculated as three times the standard deviation of the area counts from 7 to 10 chromatographic runs. It represents the lowest amount of an analyte that can be reliably detected by the instrument. This amount is then divided by the average volumes for each matrix and expressed in the tables as the lowest detectable concentration (pg/m^3 or ng/L) in a typical sample. The value is the estimated MDL. To determine the actual MDL, low-level standards need to be added to each sampling matrix and taken through the extraction and analysis procedures. This work is now underway, but the results were not available for this report. In some cases, the estimated MDL reported here is higher than the LOD. For example when none of the field blanks shows a chromatographic peak for a particular analyte, the LOD will be zero. The MDL, however, is based on a standard solution with a high enough concentration to give a detector response. The MDL will always have a positive, non-zero value and is a better estimate of the maximum contribution of the field blank to the sample in cases where the MDL is higher than the LOD.

Other column headings in the tables and the calculation of averages are described in section 2.4. The vapor-phase concentrations given for "-HCH may be too high due to the presence of interfering compounds in the air samples.

Table 8. Organic Chemicals in Air (ng/m^3) and Precipitation (ng/L) at Point Petrie[(1)]

Table 9. Organic Chemicals in Air (ng/m^3) and Precipitation (ng/L) at Eagle Harbor[(2)]

Table 10. Organic Chemicals in Air (ng/m^3) and Precipitation (ng/L) at Sleeping Bear[(3)]

Table 11. Organic Chemicals in Air (ng/m^3) and Precipitation (ng/L) at Sturgeon Point[(4)]

4. SUMMARY

This is a report of meteorological observations and chemical measurements from the U.S. sampling stations in the Integrated Atmospheric Deposition Network (IADN).

The Integrated Atmospheric Deposition Network is a joint effort of the U.S. and Canada to measure atmospheric deposition of toxic materials to the Great Lakes. It was mandated by Annex 15 (Airborne Toxic Substances) of the Great Lakes Water Quality Agreement between the U.S. and Canada. The network also fulfills the requirements of the U.S. Clean Air Act Amendments (CAAA) of 1990, which called for a Great Lakes atmospheric deposition network.

This report contains data from sampling sites at Eagle Harbor, Michigan, on Lake Superior; Sleeping Bear Dunes National Lakeshore, near Empire, Michigan, on Lake Michigan; and Sturgeon Point, near Evans Center, New York, on Lake Erie. It also contains results for samples collected for purposes of comparison with Canadian participants at the Canadian Point Petre site. A separate Canadian report will present results from the sites at Point Petre on Lake Ontario, and Burnt Harbor, on Lake Huron.

This report covers samples collected between October 1990 and December 1992. Analytes include PCBs, chlorinated pesticides, and PAHs in air and precipitation, and trace metals in air. This is a report of data only. Interpretation of the joint U.S.-Canada data set will be carried out later.

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Site coordinators and site operators are Marty Auer and James Pauer of Michigan Technological Institute at the Eagle Harbor site, Kim Irvine and Ellen Pratt of State University College at Buffalo for the Sturgeon Point site, Tom Van Zoeren and Steve Yancho of the National Park Service at the Sleeping Bear Dunes site, and Ray Hoff and Darrell Smith of Environment Canada at the Point Petre site. Ray Hoff also provided meteorological data from Point Petre.

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APPENDIX A

ILLINOIS STATE WATER SURVEY

12-30-92

IADN WEEKLY SITE VISIT CHECK LIST

1. Refer to the monthly site protocol for specific sampling dates.

2. Collect samples from the Aerochem Metrics samplers. The volume of one sample should be measured and aliquots taken for field measurement of conductivity and pH and for nutrient and trace element analysis. The 500 ml aliquot for nutrients should be put in a plastic bottle and mailed to the EPA Central Lab. The other sample (sampler with enclosed base) should be left in Teflon collection bottle and mailed with a separate GLAD data sheet to the Water Survey. Check the operation of the Aerochem Metrics samplers. Replace the plastic bags in the standard Aerochem, and the collection bottle and inlet in the modified Arochem even if no precipitation has occurred. Refer to the GLAD operators' manual for detailed procedures.

3. Collect samples and measure the volume in the MIC samplers and check the operation of the sampler and heater. Set up the MICs for the next sampling cycle. Mail XAD-2 columns and a data sheet for each sample to the Water Survey. Refer to MIC procedure sheet for details.

4. Change the tape every other week on the Campbell datalogger. The tape should be on side "A". Check the wind direction, wind speed and temperature readings weekly. Be sure to leave it in the data logging mode. Mail the tape to the Water Survey.

5. Change the filter on the TSP/TOC high-volume sampler using the glass fiber filters. Set the timer to operate on the next sampling day specified. Mail the filter and a data sheet to the Water Survey.

6. Collect filters and cartridges from the organics high-volume samplers. Replace the cartridges and filters (use the glass fiber filters). Set the timers to operate on the next sampling day specified. Mail filters, cartridges and a data sheet for each sampler to the Water Survey. Refer to Hi-Vol procedure sheet for details of TSP and organics sampling.

7. Set up or collect a pair of Teflon filters in the dichotomous sampler as specified in the monthly site protocol. Place the filters in labeled Petrie dishes and mail to the Water Survey with a data sheet. Refer to the dichot procedure sheet for details.

8. Make an entry in the site log book indicating what was done at the site. Notify the Water Survey as soon as possible if there are any problems.

Illinois State Water Survey

2204 Griffith Dr.

Champaign, IL 61820

Clyde Sweet 217-333-7191

Paul Nelson 217-244-8719

ILLINOIS STATE WATER SURVEY 12-30-92

INSTRUCTIONS FOR FILTER CHANGE WITH HIGH-VOLUME SAMPLERS

This procedure covers both the TSP and organics high-vol samplers.

1. Install a pre-weighed glass fiber filter (labeled side up) in a filter casette. Do this indoors if possible.

2. If the sampler has an exposed filter, turn on the sampler; and record the reading on the magnehelic gage after 2 min. Remove the casette with the exposed filter. Record the timer reading. Take the casette indoors and wearing plastic gloves, remove the exposed filter and fold in half lengthwise with the deposit side facing in. Wrap the filter securely in aluminum foil, label and seal in a plastic bag.

3. Install the clean filter casette and tighten the thumbscrews holding the casette to the sampler inlet.

4. Remove the exposed steel cartridge, wrap it in aluminum foil, and seal in a labeled metal can. Replace a clean cartridge in the holder (see attached diagram).

5. Record the timer reading. Test by turning on the hi-vol and allow it to run for 2 minutes. Record the reading on the magnehelic gage. Turn off the hi-vol.

6. Set the timer for the desired sampling period. Normally, the samplers should start in the morning (9:00, CST) and run for 24 hours until the following morning (9:00 CST) once every 6 days for TSP and once every 12 days for organics; or as specified in the site protocol.

7. Mail all filters and cartridges to the address below. During the summer months (June - Sept), shipment should be in insulated boxes with freezer packs. Copies of the data forms should be sent along with the samples to the address below:

Dr. Clyde W. Sweet Phone numbers:

Illinois State Water Survey

2204 Griffith Dr. Clyde Sweet 217-333-7191

Champaign, IL 61820 Paul Nelson 217-244-8719

8. Sample Codes: FILTERS nH-#(B)-YR MO DA-F

CARTRIDGE nH-#(B)-YR MO DA-C

n: E=Eagle Harbor

S=Sleeping Bear Dunes

T=Sturgeon Point

R=Point Petre

The "H" indicates sample type (a hi-vol sample). The date in the code is the date sampling ended or the day of the sampling for a midnight to midnight sample; the position marked "#" should be used to specify the sampler number at sites with more than one sampler. The final "F" or "C" refers to filter or cartridge samples. The "#" position should also include a "B" if the sample is a field blank.

ILLINOIS STATE WATER SURVEY 12-30-92

INSTRUCTIONS FOR FILTER CHANGE WITH DICHOTOMOUS SAMPLERS

1. If there are filters to be picked up, determine a final flow reading after allowing the dichot to warm up for 20 min. Remove the exposed filters from the sampler and place them into small plastic petrie dishes for transport to an indoor area.

2. For the coarse filter only, remove the Teflon filter from the yellow plastic holder and secure it in a pre-labeled "Petrie-Slide" for shipment. Mail the fine filter still in the white holder and in the small petrie dish. Label both with the appropriate sample code.

3. Install clean filters with the labeled side facing up. The filter holders are color-coded: yellow = coarse; white = fine.

4. Record the timer reading. Test by turning the dichot on and allow it to run for 20 minutes. Set the fine and coarse flow rates to the values written next to the respective flow meters. Record these as the initial flow readings. Turn off the dichot.

5. Set the timer for the sampling period specified in the monthly site protocol using the color-coded timing pins: silver = on; black = off. Some of the samplers have electronic timers with digital readouts. Normally, the sampler will run for four-day 24-hour sampling periods during the 4-week sampling cycle. The timer on the dichot is a 7-day timer, so the exposed filters must be picked up or the sampler reset within one week of the start of sampling or the sampler will start up again.

6. Mail all filters to the address below. Copies of the data forms should be sent along with the samples to the address below:

Dr. Clyde W. Sweet Phone numbers:

Illinois State Water Survey

2204 Griffith Dr. Clyde Sweet 217-333-7191

Champaign, IL 61820 Paul Nelson 217-244-8719

7. Sample codes: nDF-YR MO DA (fine)

nDC-YR MO DA (coarse)

n: E=Eagle Harbor

S=Sleeping Bear Dunes

T=Sturgeon Point

The "D" indicates sampler type (dichot); the "F" or "C" indicate the fine or coarse filter. The date in the code is the date sampling ended. Example: EDF-900820 refers to a fine "metals" sample collected at Eagle Harbor using the dichotomous sampler on Aug. 20, 1990.

ILLINOIS STATE WATER SURVEY 12-30-92

INSTRUCTIONS FOR XAD-2 COLUMN CHANGE WITH MIC SAMPLERS

1. Make sure that all precipitation has passed through the column. If rain or snow has been recent and precipitation is still eluting from the column, wait until all the liquid has drained from the funnel. If the system is plugged, catch any standing liquid in a clean pyrex beaker and pass it through the column.

2. Measure and record the total precipitation volume using the graduated cylinder.

3. Wearing plastic gloves, rinse the stainless steel collection surfaces with about 400 mL of deionized water while scrubbing with a piece of glass fiber filter (half of an 8x10" filter with serial no. removed) to remove deposited particles. Allow these rinsings to pass over the column until the water level is halfway between the top of the column and the top of the resin bed. Remove the column; cap both ends with Teflon plugs (make sure the black O-rings are in place). Seal the glass fiber filter in a sample jar; label and package the column and jar for shipment. During the winter (Nov-April), the package should be marked "do not freeze"; during the summer (Jun-Sept), shipment should be in a insulated container with ice packs.

4. Clean the collector surfaces by rinsing with 200 mL of pesticide-free methanol followed by approximately 1 liter of clean tap water with additional scrubbing. Use a test tube brush to clean the funnel outlet. This should be followed by another rinse with 200 mL of deionized water. Discard these rinsings.

5. Install a new column making sure the top and bottom O-rings are in place. After opening the outflow valve and positioning the outflow tubing (see attached diagram), add about 50 mL of deionized water to the collection funnel. Make sure that this water flows through the system; then empty the receiving jug. Wrap the column tightly with aluminum foil to exclude light.

6. Send the column and a data sheet for each sample to:

Dr. Clyde Sweet Phones:

Illinois State Water Survey Clyde Sweet 217-333-7191

2204 Griffith Dr. Paul Nelson 217-244-8719

Champaign, IL 61820

8. Sample code: nP-#(B)-YR MO DA

n: E=Eagle Harbor

S=Sleeping Bear Dunes

T=Sturgeon Point

R=Point Petre

The date in the code is the date the sample is picked up; # refers the sampler number at sites where there are more than one sampler, include a "B" in this position if the sample is a blank; P refers to sample type (precipitation).

Received* Analysis* Data*

Samples Total Month Total Month Total Month

Pt. Petre*

PUF/XAD 101 2 87 3 73 3

Filter 32 1 31 0 23 0

Precip. 38 0 38 1 30 1

Eagle Harbor*

PUF/XAD 118 4 85 2 72 9

Filter 26 1 25 1 18 0

Precip. 58 2 49 1 31 2

Dichot 20 1 16 0 8 0

Sturgeon Pt.*

PUF/XAD 69 4 58 1 33 2

Filter 18 0 18 1 10 0

Precip. 33 1 25 1 12 0

Dichot 17 1 12 0 8 0

Sleeping Bear*

PUF/XAD 73 4 54 1 33 3

Filter 20 2 15 1 9 1

Precip. 31 1 23 2 13 1

Dichot 17 0 15 0 7 0

Indiana Dunes*

XAD 11 2 9 1 0 0

Filter 3 0 3 1 0 0

Precip. 5 1 4 1 0 0

Dichot 6 1 2 0 0 0

IIT*

XAD 5 3 2 1 0 0

Filter 2 1 1 1 0 0

Precip. 3 1 1 1 0 0

Dichot 3 1 0 0 0 0

Operation dates: Pt. Petre 10-1-90 to 12-3-91 and 3-17-92 to date; Eagle Harbor 11-15-90 to date; Sturgeon Pt. 11-15-91 to date; Sleeping Bear 12-15-91 to date; Indiana Dunes 11-17-92 to date; IIT 1-15-93 to date

***RECEIVED numbers are the number of samples logged in to date and for the month; ANALYSIS numbers are the number of samples for which extraction has been completed and analysis is underway; DATA numbers are the number of samples for which final data is available. Filter samples are monthly composite samples for which 3 filters are combined. The vapor trap absorbent was PUF before 5-4-92, XAD-2 after that date. Each dichot sample consists of a fine and coarse filter.**

APPENDIX B

QUALITY ASSURANCE REPORT

Executive Summary

1.1 Introduction

The Integrated Atmospheric Deposition Network (IADN) is a joint monitoring program between the United States and Canada. The program's objectives are to determine the status, change, and trends of toxic organics in the Great Lakes. The intent of the network is to measure and evaluate the concentration of toxic pollutants in the atmosphere and their deposition (particles, vapor, and precipitation) at a regional level of detail. The network provides continuous monitoring programs with sampling and analysis year around. The Illinois State Water Survey (ISWS) provides research support to IADN for sample collection, sample analysis, method development, data management,

data interpretation, data transfer to other researchers and agencies, and quality assurance. The ISWS measures meteorological and chemical parameters as described in the Quality Assurance Project Plan (QAPjP) (Gatz, et al., 1992). The ISWS is responsible for three U.S. monitoring stations on the Great Lakes and has participated in a comparative sampling program at one Canadian station. Sampling locations are listed below:

Eagle Harbor, MI, on Lake Superior

Sturgeon Point, near Evans Center, NY, on Lake Erie

Sleeping Bear Dunes National Lakeshore, near Empire, MI, on Lake Michigan

Point Petre, Canada, on Lake Ontario (Canadian station)

Quality Assurance Program and Optimization

Binational Quality Assurance (QA) procedures and policies for the IADN have been developed and ISWS QA plans implemented. Quality assurance objectives and activities were defined in three documents: 1) Quality Assurance Program Plan (QAPP); 2) Quality Assurance Project Plan (QAPjP); and 3) Standard Operating Procedures (SOPs). These policies have been reviewed and revised periodically to accommodate changes in techniques and goals that occurred as the program evolved.

An interim Quality Assurance Program Plan (QAPP) (Brice and Hoffman, 1993) was developed in the spring of 1992. This plan is a comprehensive program-wide binational quality assurance plan. It outlines the elements of the IADN program and delineates the QA activities that are essential in order to produce data of

sufficient quality to meet the program goals. It contains information of a general nature regarding all parties involved in the IADN. The plan was reviewed and revised during 1992-1993. It is currently awaiting final review and signatures of participating agencies.

The Quality Assurance Project Plan (QAPjP) "Measurement of Toxic Atmospheric Deposition to the Great Lakes" (Gatz, et al., 1992) was initiated in December, 1991. This plan was revised, approved, and distributed in March, 1993. The plan details ISWS responsibilities associated with the IADN project.

ISWS laboratory Standard Operating Procedures (SOPs) were initiated in 1992. They were revised and redistributed periodically throughout the reporting period. Currently, laboratory SOPs are described in two manuals: 1) "Analysis of PCBs and Pesticides in Air and Precipitation Samples, Instrumental Analysis and Data Reduction " (Basu, et al., 1993); 2) "Analysis of PCBs, Pesticides, and PAHs in Air and Precipitation Samples, IADN Project, Sample Preparation Procedure" (Willett and Basu, 1993).

A draft version of sampling SOPs was distributed to all site operators and QA personnel at "IADN Operators Training Workshops" in November, 1993. A final version was distributed in December, 1993 (Sweet, 1993).

Sampling and analytical protocols were modified and improved as the project evolved. Significant protocol changes are shown below:

Sampling modifications:

February, 1992	trapping agent for organics in precipitation samples changed from Empore^{7} disks to XAD-2 resin
May, 1992	organic vapor trapping adsorbent changed from polyurethane foam (PUF) to XAD-2 resin

Laboratory modifications:

April, 1991	analytes alpha- and gamma-hexachlorocyclohexane, and dieldrin added
January, 1992	analytes DDD, DDE, DDT, and hexachlorobenzene added

Analysis of quartz fiber filter blanks showed high background levels for some PAHs and pesticides and their use was discontinued in December 1991. Background levels were not elevated for PCBs. Measurements of organics in particulate matter were not adversely affected since the TSP/TOC filter samples (collected on glass fiber filters) were utilized for the analysis. Beginning early in 1992, glass fiber filters were routinely heated to 450^{o}C before use to avoid potential contaminants.

Special studies were conducted to evaluate sample stability under conditions encountered during the project. Some of the field samples were stored at -20^{o} C for up to 12 months before the ISWS lab began analyses. In late 1992, sample stability measurements were initiated using paired (collocated) samples to determine the effects of sample storage before extraction. One of the paired samples was extracted within the storage time specified in the QAPjP (1-2 months for organics). The "twin" sample was stored for six months or one year before extraction. Results from the six months stability evaluation have been completed. Preliminary results indicated no analyte losses occurred after six months of storage at -20 C. Results from the one year stability will be available in future reports.

Since up to two weeks could elapse before samples are received from field sites, special studies were also conducted to determine the effect of field storage conditions on sample integrity. Paired (collocated) samples collected at Champaign, IL were used to determine stability of the samples under field storage conditions. One of the paired samples was frozen immediately after collection. The "twin" sample was stored at room temperature for up to two weeks. Results revealed no significant differences in analyte concentrations between the room temperature (25^{O}C) and freezer (-20^{O}C) storage conditions.

Improvements in the analytical method included: 1) adjusting the laboratory matrix spike levels to achieve concentrations which reflected those observed in the site samples; 2) increasing the number of quality control samples processed with each set of samples extracted; 3) documenting instrument linearity and detection limits for the gas chromatographic methods for all analytes; 4) analyzing reference standards (from a separate source) as instrument calibration checks; and 5) improving the chromatographic methods to obtain resolution of previously unresolved peaks and to identify interfering compounds (for example, DDE was identified as a positive interference for PCB congener 77).

Data Quality Assessment

The QAPjP (Gatz, et al., 1992) defines the measurement quality objectives (MQOs) established for this monitoring project. The MQOs are directed toward the attributes of precision, accuracy, completeness, and detectability of the analytes selected. Results of the ISWS efforts to meet the acceptance criteria for the established MQOs will be compiled and published in periodic Quality Assurance Reports.

1.3.1 Detectability

The minimum detection limit (MDL) is the lowest analyte concentration that an analytical method can reliably detect. The MDL was defined as the mean analyte concentration plus three standard deviations of data obtained from lab matrix blanks. MDLs could not be calculated for this reporting period since many lab matrix blanks yielded no detectable values for a number of analytes. An alternate method of determining the MDL using a low level calibration standard was used. When using a low level standard, the value is more correctly defined as the instrument detection limit (IDL). The IDL was obtained by performing multiple analysis of a low level standard (three separate runs of 7-10 samples per run). It is defined as three standard deviations of the data set. IDLs were calculated for all analytes and are listed in Table 4.1.

The limit of detection (LOD) is the lowest analyte concentration that can be reliably detected. LODs are affected by the uncertainty introduced during sampling, handling, preparation, extraction, and analysis. The LODs were determined for all IADN target organic analyte using field blanks for each matrix sampled. All field blanks were handled in an manner identical to the site samples. The LODs were defined as the mean analyte concentration plus three standard deviations, based on the matrix specific field blanks. Matrix specific LODs were computed for all IADN analytes. LODs are listed in Table 4.2.

1.3.2 Precision

Precision is a measure of mutual agreement among multiple measurements of the same property, usually under prescribed similar conditions. Several types of samples were collected to determine precision at various measurement phases.

Overall precision (sampling and laboratory) was evaluated with collocated field duplicates from identical samplers located at IADN master stations. The MQO for the sampling precision was based on the relative percent difference (RPD) from these paired samplers. The RPD acceptance limits were # 50% for values greater than five times the LOD and # 100% for values less than five times the LOD. The RPDs for all paired samples were compiled for each analyte for vapor cartridge (PUF and XAD-2), filter (GFF), and precipitation (Empore and XAD-2). The data are listed in Table 4.3. A summary of paired sample RPD results for all analytes follows:

	number failing the MQO	number passing the MQO	total number	
Matrix				% acceptable
all matrices	243	2444	2687	91.0
precipitation-Empore	33	76	109	69.7
precipitation-XAD-2	35	249	284	87.7
vapor cartridge-PUF	127	1324	1451	91.3
vapor cartridge-XAD-2	36	570	606	94.1
filter-GFF	12	225	237	94.9

Of the matrices investigated, the precipitation-Empore collocated samples resulted in the lowest % acceptable values. This matrix was replaced with wet XAD-2 in February 1992. RPDs with wet XAD-2 resulted in improved precision.

Laboratory precision was determined by the use of laboratory surrogate spikes (LSS) and laboratory matrix spikes (LMS). The MQO acceptance criterion for LSS and LMS precision was within 2 standard deviations of the data sets. Laboratory surrogate spikes are influenced by interferents originating from the matrices or from the samples and are not indicative exclusively of laboratory precision. Analysis of split samples may be a better indicator of this measure. Analysis of split sample results will be presented in future QA reports.

Three laboratory surrogate spikes were added to each sample extracted in the laboratory. Control charts (Figures 4.1 to 4.3) and statistical analysis from 458 surrogate spikes were compiled for the three surrogates (PCB congeners 14, 65 and 166). The relative standard deviations (RSD) for the surrogate standards were 31%, 21% and 20% for PCB 14, 65, and 166, respectively, from the 458 samples. The mean recovery " 2 SD obtained for each surrogate was :

PCB 14 mean = 95% 2 SD range = 36% to 154%

PCB 65 mean = 78% 2 SD range = 45% to 111%

PCB 166 mean = 90% 2 SD range = 53% to 127%

PCB 14 surrogate resulted in a significantly higher SD than that observed for PCB 65 and PCB 166. Early eluting PCB congeners are more subject to interferences from extraneous peaks during chromatographic analysis. This sporadic interference is reflected in the precision statistics for PCB 14 surrogate spike and in

the LOD value for PCB 5+8 , which elutes just before PCB 14 in the chromatogram (see Table 4.2). PCB 14 surrogate spike does not reflect the overall precision of the majority of the data. Other surrogates that may be better indicators of overall precision are undergoing method development and may be implemented for future reports (deuterated PAHs and pesticides).

A laboratory matrix spike was prepared and processed with each set of samples extracted (10-20 samples/set). A representative matrix (filter, dry cartridge material, or wet XAD-2) was spiked with all analytes and processed identically to the site samples. Individual analyte recovery results are listed in Table 4.4. Control charts for individual analytes are presented in Appendix A. The average recoveries for all analytes within the three target groups were:

	PCBs	Pesticides	PAHs
mean recovery (%)	94.07	95.61	79.46
mean std. dev. (%)	22.46	21.50	13.89

1.3.3 Accuracy

Accuracy is the level of agreement between an observed value and the "true" value of an analyte present in air or precipitation samples. Laboratory accuracy was evaluated with laboratory surrogate spikes (LSS), laboratory matrix spikes (LMS), interlaboratory comparison studies, and confirmation/reanalysis of selected samples performed at a separate laboratory.

Interlaboratory comparison studies for IADN participants were initiated by the Ontario Ministry of the Environment. The ISWS completed Phase I of these studies in 1992. Phase I required the determination of trace levels of metals, PCBs, pesticides and PAHs in ampouled standards for direct instrument analysis. Phase II was initiated in July, 1993, and was completed in December 1993. Phase II required the analysis of the same analytes as Phase I; however, two ampoules were standards for direct instrument analysis and two ampoules required a clean-up step before analysis. Results from the Phase I interlaboratory study are presented in Appendix B.

Laboratory surrogate spikes (LSS) were prepared by the addition of three surrogate standards (PCB congeners 14, 65, and 166) to every sample processed. The surrogate standard recovery was used to track the recovery of the analytes of interest in the individual site samples; and was used to assess overall laboratory accuracy. The MQO acceptance criterion for the average recovery of the three spiked surrogate standards was 50-130%. Ninety-eight percent of the 458 samples met this acceptance criterion. Additionally, 2/3 of the three surrogates must yield $50% and #130% recovery. Ninety-nine percent of the samples met this acceptance criterion. Control charts of lab surrogate spikes are presented in Figures 4.1 to 4.3. The mean percent recoveries " one standard deviation computed for 458 samples processed through the reporting period were:

PCB 14: 95 " 29.5%

PCB 65: 78 " 16.5%

PCB 166: 90 " 18.5%

Individual analyte recovery was determined from the laboratory matrix spikes (LMS). These data were used to assess analyte specific laboratory accuracy. Recovery data for 56 individual analytes are listed on Table

4.4. Analyte specific control charts allow for monitoring the effects of method variables over time. Control charts are presented in Appendix A. The LMS data was not sorted by matrix due to inadequate numbers of samples from some matrices to obtain meaningful statistics. Matrix specific recovery data will be available in future QA reports. Different symbols were used for each matrix on the control chart plots to allow for monitoring matrix specific differences. The MQO acceptance criterion required mean recoveries of 50-130% for all LMS samples. In addition, 70% of the individual analytes were to yield 50-130% recovery. Programs to evaluate the LMS fit to this MQO are currently being developed and those results will be presented in future reports.

Confirmation or reanalysis of selected samples was performed by the Illinois Department of Energy and Natural Resources Hazardous Materials Laboratory, Champaign, IL. Gas chromatography-mass spectroscopy (GC-MS) was used to: 1) confirm that target analytes were present, and 2) confirm that the analyte/s were present at the reported levels. Analysis by a second laboratory provided needed analytical confirmation when outlying data points were found. A positive interference was suspected for some samples yielding abnormally high results. In some instances, a positive interference was identified. The results of this analysis are being compiled and will be available in subsequent reports.

1.3.4 Representativeness

Representativeness expresses the degree to which data accurately and precisely represent characteristics of a population, parameter, variations at a sampling point, a process condition, or an environmental condition. Representativeness for this project was a measure of the parameter variation at a sampling point and was evaluated by collecting random duplicate samples. The precision data from the collocated samples presented in 4.2.1 and on Table 4.3 reflect the representativeness of the sampling system.

Sampling sites were selected to be free from local sources of contamination and to represent regional background concentrations of the target compounds. Comparison of data within and between sampling sites could, therefore, yield information useful for evaluation of representativeness criteria for this project. Data summaries for the sampling sites are currently being developed. Results will be made available in future QA reports.

The sampling, handling and analysis protocols selected were consistent with those used by other U.S. and Canadian researchers whenever practical. This allows the data generated by this project to be compared with data from previous studies and from Canadian researchers.

Site samples were analyzed in their entirety, therefore, subsampling and sample homogeneity were not a concern for this reporting period.

1.3.5 Completeness

Completeness is the measure of the numbers of samples obtained compared to the numbers that were expected to be obtained under normal conditions. The completeness goal was 90% for sampling and 95% for laboratory data reported for each sample collected. Based on sampling frequencies, and allowing for sample compositing (monthly filter composites), the target number of samples/year/site (not including

collocated duplicates) was: 25/year for vapor cartridges; 12/year for particulate filters; and 13/year for precipitation. Sample results from the four sites through December, 1992 yielded the following completeness statistics:

Percent Completeness

Target # samples Actual # samples (sampling and laboratory)

Vapor Cartridge 158 175 111 %

Particulate Filter 76 75 99 %

Precipitation 77 82 106 %

Initial start-up at all sites required sampling at increased frequencies. This resulted in completeness levels over 100%.

1.3.6 Comparability

Comparability expresses the confidence with which one data set can be compared to another. The data should be comparable within and between sites.

Within-site data comparability was assured by maintaining the same procedures throughout the duration of the project as much as was reasonable. When a procedure or an analysis was modified or changed, a comparison was made to verify that the data were identical, more precise, or more accurate than those previously obtained. Changes to SOPs required a discussion of the impact upon the study. Quality assurance and quality control samples allowed for laboratory and sampling performance to be monitored over the duration of the project.

Between-site comparability was assured by utilizing sampling and analysis methods based on procedures employed by previous atmospheric deposition projects within the Great Lakes basin (Sweet, et al., 1992). Data representativeness and comparability were also assured by using sampling, handling, and analysis protocols as similar to those used by other U.S. and Canadian researchers as practical.

The Canadian sampling station at Point Petre was used for comparison studies by ISWS and Canadian researchers. Samples collected at this site allowed for comparison of methods and sampling protocols between groups. Since the first data reports are now being generated by IADN participants, insufficient data are currently available for comparability determinations from this site.

Participation in interlaboratory studies also provide comparability data for analytical methods employed by different researchers within the IADN. Data from the Phase I interlaboratory study are presented in Appendix B.

1.4 Quality Assurance and Quality Control Samples

Quality assurance (QA) and quality control (QC) samples were incorporated into the sampling and laboratory procedures. The following QA/QC samples were included with each sample set whenever possible:

Site sample set:

One field blank (FB) per month per station for each matrix type

One pair of collocated field duplicate (CFD) samples per month from each master station for each matrix type

Laboratory sample set:

One matrix FB

One set of CFD samples

One method/laboratory blank (LB)

One laboratory matrix spike (LMS) for each matrix prepared

Additional QA/QC performance checks performed with each set of samples processed included: 1) instrument calibration checks; and 2) analysis of laboratory surrogate spikes.

Periodic QA checks included: 1) analysis of interlaboratory performance check samples; 2) parallel analysis of old and new calibration and spiking standards before use of new solutions; and 3) instrument linearity checks.

Detailed laboratory records were maintained for: 1) sampling conditions; 2) sample handling; 3) instrument maintenance and calibration; 4) standard and reagent preparation; and 5) sample preparation.

Method development work included initial investigations with deuterated PAH surrogate standards. Additionally, work to improve recovery or eliminate interferences for target organics in individual matrices was continued. Results will be detailed in future reports. Chromatographic coelution interferences were documented and identified whenever possible.

7.0 References

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Figure 1A. Surrogate Spike Control Charts

1. ***Table column headings are explained in sections 2.4 and 3.3.3.**

2. ***Table column headings are explained in sections 2.4 and 3.3.3.**

3. ***Table column headings are explained in sections 2.4 and 3.3.3.**

4. ***Table column headings are explained in sections 2.4 and 3.3.3.**